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A METHOD OF MANUFACTURING AROMATIC CARBONATES

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Abstract

Problem

The objective of the present invention is to provide a method of manufacturing aromatic carbonates.

Means to solve

In the production of aromatic carbonates by the reaction of an aromatic hydroxy compound with carbon monoxide and oxygen, the above-mentioned reaction is carried out in the presence of a catalyst consisting of (A) at least one type selected from palladium and palladium compounds, (B) at least one type selected from lead compounds, (C) at least one type selected from cerium compounds, and (D) at least one type selected from halides.

Claims

1. A method of manufacturing aromatic carbonates characterized by the fact that in the production of aromatic carbonates by the reaction of an aromatic hydroxy compound with carbon monoxide and oxygen, the above-mentioned reaction is carried out in the presence of a catalyst consisting of (A) at least one type selected from palladium and palladium compounds, (B) at least one type selected from lead compounds, (C) at least one type selected from cerium compounds, and (D) at least one type selected from halides.

2. The method of manufacturing aromatic carbonates described in Claim 1 above, in which component (D) is a bromide.

3. The method of manufacturing aromatic carbonates described in Claim 2, in which component (D) is a quaternary ammonium bromide salt.

4. The method of manufacturing aromatic carbonates described in Claim 1 above, in which the above-mentioned aromatic hydroxy compound is a phenol.

Detailed explanation of the invention

[0001]

Technical field of invention

The present invention pertains to a method of manufacturing aromatic carbonates. More precisely, the present invention pertains to a method of manufacturing aromatic carbonates by the reaction of an aromatic hydroxy compound with carbon monoxide and oxygen in the presence of a specific catalyst system. Aromatic carbonates are useful compounds when used as organic synthetic raw materials, and in particular, diphenyl carbonate is gaining attention as a raw material for polycarbonates, etc.

[0002]

Prior art

In the past, as a method of manufacturing aromatic carbonates, a method was used wherein a reaction is carried out

for an aromatic hydroxy compound and a carbonyl chloride. However, the above-mentioned method is not desirable since the toxicity of the carbonyl chloride is high. Thus, as a method without carbonyl chloride, a method of manufacturing aromatic carbonates consisting of the reaction of an aromatic hydroxy compound with carbon monoxide and oxygen has been suggested.

[0003]

As a catalyst used in the above-mentioned method, a catalyst in which a compound containing a palladium compound and a metal of group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table, and a base are used and are described in Japanese Kokoku Patent No. Sho 56[1981]-38144; a method in which a palladium compound, manganese complex, cobalt complex, a base and a desiccant are used is described in Japanese Kokoku Patent No. Sho 56[1981]-38145; a method in which a palladium compound, iodide, and a zeolite are used is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551; a method in which a palladium compound, a divalent or trivalent manganese compound, a tetralkylammonium halide and benzoquinone are used is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564; a method in which a palladium compound, cobalt compound, a tetraalkylammonium halide, and benzoquinone are used is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754; a method in which palladium or a palladium compound, a cobalt compound, halide, and an alkali compound are used is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095; a method in which a palladium compound, copper compound, benzoquinone, and onium halide are used is described in Japanese Kokai Patent

Application No. Hei 5[1993]-39247; a method in which at least one type of palladium or a palladium compound, cobalt compound, and alkali metal halide are used is described in Japanese Kokai Patent Application No. Hei 5[1993]-58961; a method in which a catalyst consisting of at least a metal cocatalyst selected from the group consisting of palladium compounds, quaternary ammonium salts, cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium, and copper, and an organic cocatalyst selected among the group of aromatic ketone, aliphatic ketone, and aromatic polycyclic hydrocarbon, are used is described in Japanese Kokai Patent Application No. Hei 5[1993]-97775; a method in which a palladium compound, a cerium compound, and a quaternary ammonium salt are used is described in Japanese Kokai Patent Application No. Hei 6[1994]-9505; a method in which a metal cocatalyst selected among the group of a palladium compound, manganese compound, cobalt and copper and a nitrile compound are used is described in Japanese Kokai Patent Application No. Hei 6[1994]-41020; a method in which a palladium compound, 5-coordinate complex of cobalt, and a quaternary onium salt are used is described in Japanese Kokai Patent Application No. Hei 6[1994]-172268; a method in which an inorganic cocatalyst selected from the group consisting of palladium compounds, cobalt, manganese and copper, and an organic cocatalyst such as a quaternary onium salt, and terpyridine are used is described in Japanese Kokai Patent Application No. Hei 6[1994]-172269; a method in which a palladium compound, a monovalent or divalent copper compound and an ammonium halide compound are used is described in Japanese Kokai Patent Application No. Hei 6[1994]-211750; a method in which an activation treatment is carried out for a precious metal catalyst with carbon monoxide

and used as a catalyst is described in Japanese Kokai Patent Application No. Hei 7[1995]-188116, a method in which a reaction is performed as removal of water generated as a result of the reaction is carried out is described in Japanese Kokai Patent Application No. Hei 7[1995]-247243; and a method in which a palladium compound, lead compound, and a quaternary ammonium or quaternary phosphonium halide are used is described in European Patent No. 0,663,388.

[0004]

Problems to be solved by the invention

However, in the prior art, a system with a high proportion of metal cocatalyst to the primary catalyst is commonly used as a catalyst. When the proportion of cocatalyst used is too high, the cost of the catalyst increases, and handling of the catalyst becomes complicated. The objective of the present invention is to provide a method of manufacturing an aromatic carbonate effectively using a catalyst with a significantly lower proportion of metal cocatalyst than is used in the prior art.

[0005]

Means to solve the problem

As a result of much research carried out by the present inventors, it is possible to produce aromatic carbonates effectively even when a catalytic system with a significantly lower proportion of metal cocatalyst is used in a system wherein

a lead compound is used as the metal cocatalyst when a cerium compound is used in combination, and the core halogenation of the aromatic hydroxy compound can be reduced significantly compared with a catalytic system that does not use cerium, and the present invention was accomplished. In other words, the present invention is a method of manufacturing aromatic carbonates characterized by the fact that in the production of an aromatic carbonate by the reaction of an aromatic hydroxy compound with carbon monoxide and oxygen, the above-mentioned reaction is carried out in the presence of a catalyst consisting of (A) at least one type selected from the group consisting of palladium and a palladium compound, (B) at least one type selected from among the group consisting of lead compounds, (C) at least one type selected from the group consisting of cerium compounds, and (D) at least one type selected from the group consisting of halides. In the following, the present invention is explained in further detail.

[0006]

Embodiment of the invention

1. Reaction raw materials

(1) Aromatic hydroxy compound

The aromatic hydroxy compound used in the present invention is an aromatic mono- or polyhydroxy compound, and phenols, substituted phenols such as cresol, xylenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, and

dibromophenol and isomers thereof, substituted naphthols such as naphthol, methyl naphthol, ethyl naphthol, chloronaphthol, and bromonaphthol, and isomers thereof, a variety of bisphenols such as 2,2-bis(4-hydroxyphenyl)propane, a variety of biphenols, a hydroxy group-substituted heteroaromatic compound having a structure such as a pyridyl or quinolyl substituted with at least one hydroxy group and isomers thereof, and substitutents thereof further substituted with an alkyl group, a halogen, etc., can be used effectively.

[0007]

(2) Carbon monoxide

For the carbon monoxide used in the present invention, a highly pure form as well as one diluted with an appropriate amount of other gases that do not have an adverse effect on the reaction such as air, argon, and carbon dioxide can be used.

[0008]

(3) Oxygen

For the oxygen used in the present invention, a highly pure form as well as one diluted with an appropriate amount of other gases that do not have an adverse effect on the reaction such as air, argon, and carbon dioxide can be used.

[0009]

2. Catalyst

The catalyst used in the reaction of the present invention comprises a combination of at least one type selected from each of component groups (A)-(D) below, and includes the four components (A)-(D) shown below.

(A) Palladium or palladium compound

The palladium or palladium compound used in the present invention is a deposited palladium such as palladium black, palladium carbon, palladium/alumina and palladium/silica, inorganic salts of palladium such as palladium chloride, palladium bromide, palladium iodide, palladium sulfate, and palladium nitrate, organic acid salts of palladium such as palladium acetate, and palladium oxalate, etc., can be mentioned. Furthermore, acetyl acetonate palladium(II), palladium complex salts wherein carbon monoxide, nitriles, amines, phosphines, and olefins are coordinated with palladium, for example, $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$, $Pd(CO)(PPh_3)_3$, $[Pd(NH_3)_4]Cl_2$, $Pd(C_2H_4)(PPh_3)_2$, $[(\eta^3\text{-}C_3H_5)PdCl]_2$, $Pd(DBA)_2$, $Pd_2(DBA)_3 \cdot CHCl_3$ (Ph = phenyl group, DBA = dibenzylidene acetone), etc., a mixture of compounds capable of producing the above-mentioned complex in the reaction system and palladium, etc., can be used. The amount of the palladium component used in the reaction is preferably in the range of 10^{-7}-10^{-2} for the aromatic hydroxy compound in terms of molar ratio, and the range of 10^{-6}-10^{-3} is especially desirable.

[0010]

(B) Lead compound

For the lead compound used in the present invention, those soluble under the reaction condition are desirable, and lead oxides such as PbO, Pb_3O_4, and PbO_2, organic acid salts of lead such as $Pb(OAc)_2$, $Pb(OAc)_4$, $Pb(C_2O_4)$ and $Pb(OCOC_2H_5)_2$, inorganic salts of lead such as $Pb(NO_3)_2$, and $PbSO_4$, etc., alkoxy lead and aryloxy lead such as $Pb(OMe)_2$ and $Pb(OPh)_2$, complex compounds of lead such as phthalocyanine lead, etc., can be mentioned for example. The amount of lead component used for the reaction is preferably in the range of 0.5-5 for component (A), and in the range of 1-3 is especially desirable.

[0011]

(C) Cerium compound

The cerium compound used in the present invention is a trivalent and tetravalent cerium compound, and inorganic salts such as cerium chloride, cerium bromide and cerium nitrate, organic acid salts such as cerium acetate, and cerium oxalate, a coordination compound of cerium such as cerium acetyl acetonate, and cerium tropolonate [transliteraton], can be mentioned as examples. The amount of the cerium compound should be in the range of 0.5-5, or preferably in the range of 1-3, in molar ratio with respect to component (A).

[0012]

(D) Halide

The halide that can be effectively used in the method of manufacturing of the present invention is not especially limited as long as a halogen salt is used, and for example, quaternary ammonium halides, quaternary phosphonium halides, alkali metal halides and alkaline-earth metal halides can be mentioned. A suitable material in this case is a quaternary ammonium halide, and is a compound represented by general formula (I)

[0013]

[Structure 1]

$$R^1R^2R^3R^4N^+X^- \quad (I)$$

[0014]

(wherein, R^1-R^4 are each alkyl groups or aryl groups with 1-10 carbon atoms, and the groups may be the same or different, X is a halogen atom). In this case, a bromide is especially desirable, and in specific terms, a quaternary ammonium salt such as tetra-n-butylammonium bromide, and tetramethylammonium bromide can be mentioned. The amount of the halide used for the reaction is not especially limited, and 10^{-4}-1 molar ratio for aromatic hydroxy compounds is desirable, and in the range of 10^{-3}-10^{-1} is especially desirable.

[0015]

3. Reaction condition

The reaction can be carried out by adding the above-mentioned aromatic hydroxy compound and a catalyst consisting of the above-mentioned components (A)-(D) to a reactor, applying pressure with carbon monoxide and oxygen while thorough stirring is provided under heat. In general, the absolute pressure during the above-mentioned reaction is in the range of 1-500 atm in terms of total pressure, and in the range of 1-250 atm is further desirable. From the standpoint of safety, it is desirable for the ratio of the carbon monoxide and oxygen composition to be outside the explosive range. The reaction temperature is in the range of 20-300ºC, and in the range of 80-250ºC is especially desirable. The reaction time varies depending on the reaction conditions used, and in general, it is in the range of several minutes to several hours. Aromatic diols such as hydroquinone or benzoquinones, which are oxide products thereof, [and] organic additives such as amines that are commonly used in conventional catalytic systems can be included during the reaction. Furthermore, for the inert solvent, hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, acetonitrile, nitrobenzene, etc., can be used.

[0016]

Application examples

In the following, the present invention is explained further in specific terms with application examples and comparative examples but the present invention is not limited to these examples within their range. In this case, the reaction product characteristics were examined by means of gas chromatographic analysis (product of SGE Co., capillary column BPX-5, 50ºC→300ºC) wherein pentadecane was used as the internal standard.

[0017]

Application Example 1

12.23 g (130 mmol) phenol, 10.22 mg (4.8 µmol Pd) 5% palladium/carbon (product of N.E. Chemical Co.), 1.07 mg (4.8 µmol) lead oxide(II), 1.52 mg (4.8 µmol) cerium acetate(III) monohydrate, and 154.06 mg (1.0 mmol) tetrabutylammonium bromide were poured into an autoclave made of Hastelloy and having an internal capacity of 50 mL, purging of the system was carried out with carbon monoxide, and 60 atm of carbon monoxide and 30 atm of dry air were supplied, and stirring was performed for 3 h at 100ºC by means of a stirring device. A quantitative analysis of the liquid phase was done by gas chromatography after the reaction. As a result, diphenyl carbonate was produced at a yield of 4.46% (2.91 mmol) for the phenol. Production of by-product bromophenols (total of ortho, para and meta members

was not observed, the same applied below) was observed at a ratio of 19.0% (0.190 mmol) for the tetrabutylammonium bromide used.

[0018]

Comparative Example 1

In the above-mentioned Application Example 1, cerium acetate (III) monohydrate was omitted, and the process was carried out as above. As a result, diphenyl carbonate was produced at a yield of 1.81% (1.18 mmol) for the phenol. Production of by-product bromophenols was observed at a ratio of 71.5% (0.715 mmol) for the tetrabutylammonium bromide used.

[0019]

Comparative Example 2

In Application Example 1 above, lead(II) oxide was omitted, and the process was carried out as above. As a result, diphenyl carbonate was produced at a yield of 2.65% (1.72 mmol) for the phenol. Production of by-product bromophenols was observed at a ratio of 16.6% (0.166 mmol) for the tetrabutylammonium bromide used.

[0020]

Effect of the invention

As shown by the results above, a significant reduction in the catalytic component is made possible, and nuclei halogenation of the aromatic hydroxy compound can be controlled. Thus, the industrial value of the method of the present invention is very high.

Translated from Japanese by the Ralph McElroy Co., Custom Division
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